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DETONATION SYNTHESIS OF CUPRITE WITH A CUBIC FACE-CENTERED LATTICE (A REVIEW)

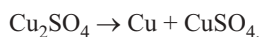
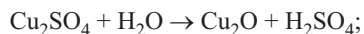
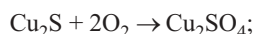
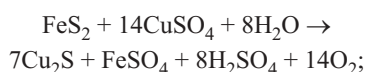
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Tenorite and a previously unknown modification of cuprite having a cubic face-centered lattice with $a = 12.078 \text{ \AA}$ are synthesized in reactions between the products of detonation of $\text{C}_4\text{H}_4\text{N}_8\text{O}_{14}$ and copper. Roentgenometric data on copper oxides identified are supplied.

Three minerals of copper oxide are known: cuprite Cu_2O , tenorite CuO , and paramelaconite Cu_4O_3 .

Cuprite in natural conditions is an intermediate product in the zone of oxidation of chalcopyrite CuFeS_2 , chalcosine Cu_2S (low-temperature hydrothermal mineral), and other copper-sulfide ores.

Cuprite produces granulated formations, less frequently aggregates of octahedral, cubic, and rhombododecahedral crystals, often merged with crystals of native copper, malachite, and lapis lazuli. It is believed that cuprite and native copper can be formed in hydrolysis of univalent copper sulfate that is formed from chalcosine under a restricted access of oxygen. The phase transformations of sulfate minerals, which may lead to the formation of cuprite are presented below [1]:



Iso- and heterovalent isomorphism is manifested in oxides with the ionic bond. Oxides with the covalent bond, namely, cuprite, quartz, cassiterite have high purity and usually have a composition close to their theoretical formulae. Tenorite is found in the form of dust and films on oxidized surfaces of native copper.

Cuprite in laboratory conditions is produced by electrolysis of NaCl solution using copper electrodes at a temperature not higher than 70°C and also by heating CuO to 1100°C

and reducing (by means of hydrazine, glucose) CuSO_4 in an alkaline solution.

CuO oxide is formed in heating Cu_2O in an air medium up to $400 - 500^\circ\text{C}$ and $\text{Cu}(\text{OH})_2$ to a temperature of 200°C . Copper oxides (Cu_2O and CuO) are widely used in reactions of oxidation of CO and lower non-saturated carbohydrates and also as pigments for glass, ceramics, and glazes.

Materials in the crystalline state form a great number of different structural types. Structural types with the tetrahedral coordination of atom are divided into two groups: a group with exclusively tetrahedral coordination and a group with another coordination. Each of these groups can be divided into two subgroups: structures incorporating into dense packing of equal-size atoms and structures not related to these packings. Structures, in which exclusively tetrahedral vacancies are filled are derivatives of only two densest packings: two- and three-layer. Formula RX_2 correlates with the complete replacement of tetrahedral vacancies, formula RX correlates with replacement by half, etc.

Cuprite, in particular, has the type is based on ABC packing [2]. Oxygen atoms in cuprite are surrounded by copper atoms along a regular tetrahedron and there are two "molecules" of Cu_2O ($Z = 2$) per cell. Complex $\bar{4}3m$ (symmetry of tetrahedron) exists only in symmorphous groups of class $\bar{4}3m$ and such halohedral groups, in which the third position plane is a mirror plane. Such complex is a duplex in I -group of class $\bar{4}3m$ and P -groups of class $m\bar{3}m$. There are no duplex or quadruplex positions for copper atoms in I -group of class $\bar{4}3m$. Complex $\bar{4}3m$ in the Fedorov group $\text{Pm}\bar{3}m$ is superimposed by complex $m\bar{3}m$. It is impossible to describe the cuprite structure in these Fedorov symmetry groups. Only Fedorov group $\text{Pn}\bar{3}m$ corresponds to the structural type Cu_2O .

Fedorov group $\text{Pn}\bar{3}m$ has two variants of arrangement of four copper atoms and two oxygen atoms. In the first variant, copper atoms are distributed in the lattice in the way to cre-

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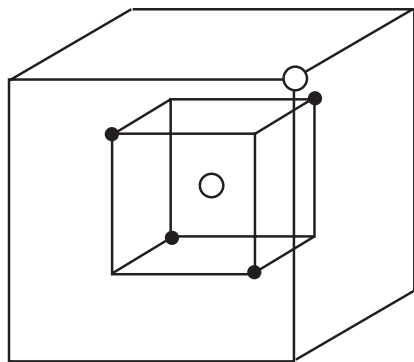


Fig. 1. Arrangement of atoms in the lattice of cuprite structure Cu_2O : ○) oxygen; ●) copper.

ated a densest three-layer cubic ABC packing: copper atoms form a face-centered lattice and oxygen atoms exist in two out of eight tetrahedral vacancies located along the volume diagonal of the cube. The coordinates of the copper atoms are 0, 0, 0; 0, 1/2, 1/2; 1/2, 0, 1/2; 1/2, 1/2, 0, and coordinates of the oxygen atoms are 1/4, 1/4, 1/4; 3/4, 3/4, 3/4. Coordination polyhedrons are the tetrahedron OCu_4 and linear coordination CuO_2 . In the second variant, oxygen atoms form a volume-centered lattice, in which copper and oxygen atoms are joined in the same way as silicon and oxygen atoms in cristobalite. The positions of silicon atoms are taken by oxygen, and the position of oxygen atom are taken by copper atoms. In this lattice copper atoms occupy centers of four out of eight little cubes into which the volume-centered cubic lattice can be split. The coordinates of copper atoms: 1/4, 1/4, 1/4; 1/4, 3/4, 3/4; 3/4, 1/4, 3/4; 3/4, 3/4, 1/4; the coordinates of oxygen atoms: 0, 0, 0; 1/2, 1/2, 1/2 (Fig. 1). This lattice is the one that is usually selected.

In cuprite the distance $\text{O}-\text{Cu}-\text{O}$ is equal to 3.7 Å and in cristobalite the distance $\text{Si}-\text{O}-\text{Si}$ is significantly shorter: 3.1 Å. The lattice of Cu_2O has low density: it has so much vacant space that inside the volume taken by the first sublattice there is enough space for a second lattice, same as the first one. They are not directly connected by the bonds $\text{Cu}-\text{O}$. Each lattice transforms into the other in translation to (0, 0, 1/2). This is what differs the Cu_2O structure from other inorganic compounds with formula RX_2 .

The parameters of the cuprite lattice are: $a = 4.2520 - 4.6296$ Å, $Z = 2$, experimental density 6.14 g/cm³, melting point 1235°C (PDF JCPDS 01-1142, 03-0892, 03-0898, 05-0667). Along with the known band of Cu_2O , additional weak bands were registered on the diffraction pattern (PDF JCDs 05-0667). There are data (PDF, JCPDS 02-1067) reporting that the diffraction pattern of cuprite corresponds to a cubic lattice with $a = 6$ Å.

The study of the dependence of sheer modulus C_{44} and $C' = (C_{11} - C_{12})/2$ of monocrystalline cuprite $\text{Cu}_2\text{O(I)}$ at the room temperature on pressure (up to 3 GPa) suggested that as the pressure increases, the stability of the Cu_2O lattice decreases [3]. Later these data were extrapolated to higher pres-

ures in [4]. It was found that under pressure of about 13 GPa, a loss of stability of the lattice based on modulus C' can be related to the formation of a new denser modification. The loss of stability based on modulus C_{44} should take place under pressure of about 17.5 GPa. Later the phase transformations of cuprite $\text{Cu}_2\text{O(I)}$ at room temperature were studied by the x-ray analysis up to pressure of 16 and 24 GPa [5, 6]. Two phase transformations were registered in [5]: at 5 GPa, $\text{Cu}_2\text{O(I)} \rightarrow \text{Cu}_2\text{O(Ia)}$ and at 12 GPa, $\text{Cu}_2\text{O(Ia)} \rightarrow \text{Cu}_2\text{O(II)}$.

The diffraction pattern of $\text{Cu}_2\text{O(Ia)}$ correlates to the cubic lattice of cuprite with $a = 4.217$ Å. The roentgenometric data for a new phase of $\text{Cu}_2\text{O(II)}$ are presented. At a pressure of 15 GPa decomposition of Cu_2O into CuO and Cu was observed.

According to the data in [6], the phase $\text{Cu}_2\text{O(I)}$ with the cuprite structure persists up to pressure of 10 GPa, the parameter of lattice $\text{Cu}_2\text{O(I)}$ under this pressure decreases from 4.27 to 4.18 Å.

At 10 GPa transformation of $\text{Cu}_2\text{O(I)}$ into $\text{Cu}_2\text{O(II)}$ was observed. The diffraction pattern of $\text{Cu}_2\text{O(II)}$ correlates with a hexagonal lattice with $a = 2.90$ Å, $c = 19.31$ Å [6]. At 18 GPa the lattice parameters decrease: $a = 2.82$ Å, $c = 19.04$ Å. Within a pressure interval of 13 – 19 GPa, gradual transformation of $\text{Cu}_2\text{O(II)}$ into a new phase, namely, $\text{Cu}_2\text{O(III)}$ with a structure of the CdCl_2 type was registered.

The known phase diagrams of binary allow systems (A. Hansen, K. Anderko, and F. Shark) represent cuprite at temperatures below 473 or 648 K as an unstable phase. However, it was established in [4] that cuprite is a thermodynamically stable phase up to 0 K and decomposes under high pressure into Cu and CuO at a temperature above 150 K.

Data on the range of homogeneity of cuprite are quite contradictory. Cuprite in the state of thermodynamics equilibrium always experiences a deficit of metal and at 1000°C exists in the range of composition $\text{Cu}_{1.9960}\text{O} - \text{Cu}_{1.9994}\text{O}$.

As a result of oxidation of thin copper films at 100 – 200°C under oxygen pressure of 100 mm mercury column, a metastable phase of $\text{CuO}_{0.67}(\text{Cu}_{1.492}\text{O})$ of thickness up to 1085 Å was obtained in [7]. X-ray analysis of $\text{Cu}_{1.492}\text{O}$ registered reflections of the cuprite lattice with hkl 110, 111, 200, 220, and 311. Electron-graphic analysis in addition to the above reflection identified as well reflections with hkl 211, 400, and 331. The lattice parameters of $\text{Cu}_{1.492}\text{O}$ and interplanar distances are not reported in [7]. Due to a high concentration of cation vacancies, $\text{Cu}_{1.492}\text{O}$ has very high paramagnetic sensibility.

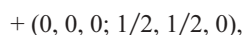
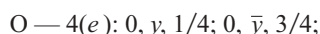
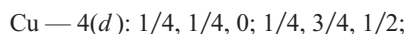
Due to the presence of cation vacancies, cuprite is a semiconductor of the p -type. Conductance activation energy is 1.5 eV.

Ya. I. Frenkel' predicted the possibility of existence of excitons in semiconductors. According to Ya. I. Frenkel's theory exciton is regarded as a conductance electron reacting with a positive hole in the form of a quasihydrogen atom, which has to have a hydrogen-like energy spectrum. Copper oxide (Cu_2O) became the first object for studying general

properties of excitons: in studying the inner photo effect, exciton series were for the first time discovered in its spectrum.

Excitons have been studied in a great number of compounds with various structures and various chemical forces in interatomic reactions. However, up to date no analog of cuprite that has a great number of hydrogen-like states has not been discovered [8].

The tenorite structure represents a distorted type of the NaCl structure [9]. Its lattice parameters are: $a = 4.685 \text{ \AA}$, $b = 3.426 \text{ \AA}$, $c = 5130 \text{ \AA}$, $\beta = 99.55^\circ$, $Z = 4$, experimental density 6.450 g/cm^3 , Fedorov group $C2/c$ (PCD ICPDS 49-0937). The atoms Cu and O occupy quadruplex positions. The symmetry of the first (invariant) position is $\bar{1}$ and the of the second (monovariant) position is 2:



where $y = 0.584$.

Melting of CuO occurs at a temperature of 1335°C with simultaneous dissociation into Cu_2O and oxygen. Copper oxide (CuO) is a phase with oxygen deficit. The CuO structure in many aspects differs from MeO crystallizing in the structural type of NaCl.

Oxygen in the tenorite structure forms a plane-square coordination around the copper atom of CuO_4 and copper forms a distorted tetrahedral coordination around the oxygen atom OCu_4 . The formation of a plane square is the result of the Jahn–Teller effect typical of Cu^{2+} , when two oxygen atoms along the axis c are lost. In this case a possible tetrahedron transforms into a square. Tenorite is a semiconductor of the p -type with a sufficiently narrow prohibited zone.

Paramelaconite Cu_4O_3 is a rare mineral crystallizing in the tetrahedral syngony. Its elementary cell parameters: $a = 5.837 \text{ \AA}$, $c = 9.932 \text{ \AA}$, $Z = 34$, Fedorov symmetry group $I4_1/amd$. Copper atoms in paramelaconite exist in two valence states: Cu^+ and Cu^{2+} . The structure Cu_4O_3 is a transitional between the structures of cuprite and tenorite. It can be described as the densest cubic packing of copper atoms with oxygen atoms in the tetrahedral vacancies. Cations Cu^+ exist in the duplex coordination, similarly to the cuprite structure, and cations Cu^{2+} exist in a plane quadruplex, nearly quadratic environment of oxygen. The crystal-chemical formula of paramelaconite is $\text{Cu}^{2+}_8\text{Cu}^+_8\text{O}_{12}$ [10]. Apart from oxide minerals Cu_2O , CuO, and Cu_8O , copper with oxygen forms incorporation phases: Cu_4O , Cu_8O , Cu_{64}O . These phases crystallized in the rhombic syngony in the primitive and base-centered lattices. The lattice parameters of Cu_4O are: $a = 4.02 \text{ \AA}$, $b = 5.66 \text{ \AA}$, $c = 5.94 \text{ \AA}$, Fedorov group $Pmm2$; Cu_8O : $a = 5.48 \text{ \AA}$, $b = 6.02 \text{ \AA}$, $c = 9.34 \text{ \AA}$, Fedorov group $Amm2$; Cu_{64}O : $a = 9.74 \text{ \AA}$, $b = 10.58 \text{ \AA}$, $c = 16.20 \text{ \AA}$, Fedorov group $Bmm2$.

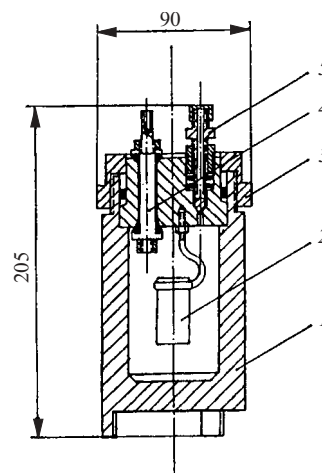


Fig. 2. Small-size explosive calorimeter bomb: 1) case; 2) copper vessel for placing explosive; 3) lid; 4) insulated electric cable; 5) needle valve for vacuum treatment.

The present paper gives the results of x-ray study of copper oxides formed in detonation of a charge of bis-(2,2,2-trinitroethyl) nitramine $\text{C}_4\text{H}_8\text{O}_{14}$ (oxygen balance + 16.5%) [11] in two experiments. In the first experiment a cylindrical charge of $\text{C}_4\text{H}_8\text{N}_8\text{O}_{14}$ of bulk density $0.8 - 0.9 \text{ g/cm}^3$ and weight 1.55 g was enclosed in a thick-walled copper shell (the weight of the shell 65 g). In the second experiment, products of explosion of homogeneous mixture $\text{C}_4\text{H}_8\text{N}_8\text{O}_{14}$ with 15 wt.% finely disperse copper powder were investigated. The charge consisting of this mixtures weighing 2 g was placed in a copper shell as well. Experiments were carried out in a specially designed vessel made of steel 12Kh18N10T of capacity 200 cm^3 (Fig. 2) of the small-scale explosive calorimeter in vacuum. The residual air pressure was $3 - 5 \text{ Torr}$ mercury column. Detonation was initiated by a charge of lead azide of weight 0.1 g .

The finely disperse preserved products of detonation were investigated in a focusing monochromator chamber FR-552 at $\text{CuK}_{\alpha 1}$ radiation (germanium as inner reference standard). The roentgenometric data of the products of detonation of $\text{C}_4\text{H}_8\text{N}_8\text{O}_{14}$ in the copper shell are listed in Table 1 and the products of the explosive mixture in Table 2.

Comparative analysis of data presented shows that during the first experiment cuprite was formed in more substantial quantity than tenorite. The identified lines of tenorite were indexed in the Fedorov group $C2/c$, $a = 4.6958(66) \text{ \AA}$, $b = 3.4263(37) \text{ \AA}$, $c = 5.1250(82) \text{ \AA}$, $\beta = 99.66(10)^\circ$. The diffraction pattern of cuprite was more complicated than the patterns listed in the database PDF ICPDS: we identified two low-intensity lines in the low-angle range: 6.973 and 3.4878 \AA . It should be noted that the tenorite band 2.3246 \AA (hkl 111) has higher intensity than the most intense line 2.5238 \AA (hkl 002, -111). Accordingly, we assumed that the band with interplanar distance 2.3246 \AA is presumably a third superstructural line of cuprite. Apparently, superimpo-

TABLE 1

Intensity, rel. units	Interplanar distance, D_e , Å		hkl of cuprite
	cuprite	tenorite	
1	6.9730*	—	111
1	3.4878*	—	222
1	3.0222	—	004
20	—	2.5238	—
100	2.4647	—	224
30	2.3246*	2.3246	115, 333
50	2.1354	—	404
1	—	1.8705	—
40	1.5075	—	008
1	—	1.3770	—
1	—	1.3047	—
10	1.2875	—	664

* Superstructural lines.

sition of this line on the tenorite line with $hkl = 111$ increased somewhat its intensity. Formally the cuprite lines (Table 1) can be indexed in cubic syngony with a face-centered lattice with $a = 12.087$ Å, $V = 1762$ Å³. The parameter a is $2\sqrt{2}$ times greater than the lattice parameter a_0 (4.270 Å) and two times higher than the lattice parameter indicated in PCD JCPDS database (02–1067). The indexing criteria $M(8) = 42$, $F(8) = 9$.

Another variant of indexation of cuprite lines is possible as well: in the tetragonal volume-centered lattice with $a = b = 2a_0 = 8.544(3)$ Å and $c = 2\sqrt{2}a_0 = 12.064(5)$ Å, $V = 880.5$ Å³. The indexation criterion $M(8) = 133$, $F(8) = 29$. The transition from a cubic lattice to a tetragonal volume-centered one is determined by the matrix:

$$\begin{vmatrix} 0 & 0 & -1 \\ 1/2 & -1/2 & 0 \\ -1/2 & -1/2 & 0 \end{vmatrix}.$$

An increase in the lattice parameters takes place either due to shift of atoms from ideal positions, or due to an ordered arrangement of atoms of different types according to a regular systems of points occupied by atoms of the same type within the system. It can be assumed that ordering of vacancies took place in the cation sublattice with preservation of the cubic symmetry.

Probably in detonation of $C_4H_4N_8O_{14}$ the cuprite phase was formed in the thick-walled copper shell as a consequence of reaction of the thin layer of the products of explosion adjacent to the shell walls with excessive copper originated as a result of its dynamic destruction. A sharp decrease in the detonation wave pressure caused preservation of the nonequilibrium composition of the explosion products.

In the second experiment, cuprite and tenorite were formed in equal quantities (Table 2). The tenorite lattice pa-

TABLE 2

Intensity, rel. units	Interplanar distance, D_e , Å	
	cuprite	tenorite
14	3.0283	—
14	—	2.7540
100	—	2.5257
86	2.4647	—
88	—	2.3170
43	2.1339	—
14	—	1.9584
43	—	1.8708
29	—	1.5805
43	1.5110	—
43	—	1.5049
33	—	1.4150
36	—	1.3739
3	—	1.3034
29	1.2881	—
29	—	1.2621

rameters: $a = 4.701(8)$ Å, $b = 3.416(4)$ Å, $c = 5.125(9)$ Å, $\beta = 99.67(12)^\circ$, $V = 81.1$ Å³, the cuprite parameters: $a = 4.272(2)$ Å, $V = 78$ Å³.

Thus, we were able for the first time during detonation of $C_4H_4N_8O_{12}$ in a copper shell to obtain copper oxides, namely, tenorite and an earlier unknown modification of cuprite in a prevailing quantity.

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